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(54) Melt-spinning process.

(57) A process for producing thermoplastic polymer fibres by melt-spinning, characterized in that an alternating copolymer of an olefinically unsaturated compound and carbon monoxide, having a molecular weight of at least 2000, is melt-spun at a temperature of at least (T+20) K and the fibre is subsequently stretched at a temperature of at most (T-10) K, in which T is the crystalline melting point of the polymer. The fibres thus spun are suitable as tyre reinforcements.

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MELT-SPINNING PROCESS

The invention relates to a process for producing thermoplastic polymer fibres by melt spinning, and to tyres comprising fibres thus spun.

Melt-spun thermoplastic fibres can be applied in the manufacture of car tyres and today large tonnage quantities are consumed in that market. Large volume polymers for this application are polyamides and polyesters, whereas polypropylene fibres can be employed as well. However, per tyre a fairly large quantity of fibre has to be used relative to the amount of elastomer. This is due to balance of properties of the aforesaid polymers which balance is mainly governed by the combination of tensile strength, flex-modulus and adhesion to rubber. In view thereof it is not possible to reduce the amount of fibre per tyre without paying the penalty of adversily affecting the quality of the tyre, thus making the tyre unsuitable for most of the market applications. Other thermoplastic fibres such as polyaramide (available under the trademarks KEVLAR or TWARON) or gel-spun high mol. weight polyethylene might be better suited in this respect, however, they are far too expensive to find their way in the tyre manufacturing industry.

The Applicants have found that another type of thermoplastic polymers, viz. alternating copolymers of an olefinically unsaturated hydrocarbon and carbon monoxide, has a very promising potential for solving the problem of reducing the relative weight of fibre to be employed for tyre manufacturing.

Compared with polyamides, polyesters or polypropylene, melt-spun fibres made of the aforesaid alternating copolymer type show an improved balance of combined tensile strength, flex modulus and adhesion to rubber, provided the melt-spinning and stretching of the fibre is implemented at certain critical temperature conditions.

The present invention is concerned with a process for the production of thermoplastic polymer fibres, characterized in that an alternating copolymer of carbon monoxide and an olefinically unsaturated compound, this polymer having an average molecular weight of at least 2000, is melt-spun at a temperature of at least (T+20) K, and the fibre is subsequently stretched at a temperature of at most (T-10) K, in which T is the crystalline melting point of the polymer.

Preferably, the stretching is effected at a stretching ratio of at least 3:1, more preferably at least 7:1, and at most 15:1. Preferred stretching temperatures are those of at least 40 K below the crystalline melting point of the polymer and preferred melt-spinning temperatures are those of at least 40 K above the crystalline melting point of the polymer.

The term "fibre" wherever used in this specification includes mono- and multifilaments in addition to fibres. The term "alternating" copolymer refers to those copolymers in which the CO-units in the macromolecules are in alternating arrangement in respect of the units derived from the olefin. Thus, in the macromolecular chains, each CO-unit is positioned next to a single unit of olefin, e.g. ethylene. The copolymer can be a true copolymer of carbon monoxide and one particular olefin, preferably ethylene or they can be copolymers of carbon monoxide and more than one olefin, e.g. ethylene and propylene. In the latter case ethylene is preferably employed as the major olefin. The relevant alternating copolymers are known per se, for example from EP-A-121965, EP-A-213671, EP-A-229408 and US-A-3914391, likewise, their methods of preparation by catalytic copolymerization are known from these references. Suitable polymerization catalysts are based upon palladium phosphine systems. Use of other known ethylene CO copolymers which do not display an alternating structure and which are produced using free radical catalysts, is not contemplated in this invention.

Usually the copolymers have a molecular weight between 1000 and 500,000.

Preferably the copolymers should have an average molecular weight of at least 5000, more preferably at least 8000. Especially good results are obtained with those of molecular weight from 10,000 to 50,000.

The physical properties of the "polyketone" polymers will depend in part on the molecular weight of the polymer, whether the polymer is a copolymer or a terpolymer and the relative proportion of the second hydrocarbon present in the case of terpolymers.

Typical melting points for such polymers are from about 175 °C to about 300 °C, more typically from 180 °C to 280 °C.

Useful polymers for the novel fibres have limiting viscosity numbers (LVN) as measured by the method wherein the polymer is dissolved in metacresol at 60 °C; using a standard capillary viscosity measuring device such as a Cannon-Ubbelohde viscometer, in the range of 0.5 to 10 LVN and more preferably 0.8 to 4 LVN and most preferably 0.8 to 2.5 LVN.

Melt-spinning and stretching of the fibre can be carried out with equipment that is currently available on the market.

The fibres produced with the process of this invention have a markedly improved ITS.IM product as compared with fibres produced from polyamides, polyester or polypropylene. In this product ITS represents the factor of improvement of tensile strength and IM represents the factor of improvement of modulus. The comparison is made whilst employing identical stretching ratios to typical fibre grades of the various thermoplastics. The improvement is recorded relative to the same property determined with non-stretched, conventional compression moulded test specimina.

Particularly suitable thermoplastic polymers to be employed in the process of this invention are copolymers of ethylene and carbon monoxide, and terpolymers of ethylene, propylene and carbon monoxide, preferably those in which the ethylene to propylene molar ratio in the polymer chains is at least 3:1. Other suitable terpolymers are terpolymers of ethylene and carbon monoxide with butene, pentene, hexene, heptene, octene, nonene, decene, dodecene, styrene, methyl acrylate, methylmethacrylate, vinylacetate, undecenoic acid, undecenol, 6-chlorohexene, N-vinyl-pyrrolidon and diethylester of vinylphosphonic acid, provided the molar ratio of ethylene to other unsaturated monomer in the polymer macromolecules is at least 3:1, preferably at least 8:1.

The fibres according to the invention are very suitable too for the preparation of polymer mats. Such mats, especially spun-bonded non-woven mats, may be used, for example, as the reinforcing layer in rolled roofing membranes prepared from modified bitumen. Such roofing membranes are superior to known polyester-reinforced roofings because the fibres show higher mechanical strength and better adhesion to the bitumen. Another useful application of these mats, particularly when woven into a fabric or mesh, lies in the preparation of a so-called geotextile, that is a permeable synthetic membrane specifically designed to be used as a construction material in civil engineering situations such as roads, drains, riverbanks, coastlines, embankments and so on. It appears that geotextiles made from the fibres according to the invention, suitably including a UV-stabiliser, have the required tensile strength, E-modulus, water permeability and soil tightness.

Example 1

Comparative tests were carried out with melt-spinning of current commercial fibre grades of Nylon-6 (N-6), polypropylene (PP) and with a fibre grade of an alternating copolymer of carbon monoxide, ethylene, and, based upon ethylene, 8 mol% of propylene ethylene (CE). The polyamide had a molecular weight of from 10,000 to 25,000, the polypropylene grade had a melt index of 20 dg/min and the copolymer had a molecular weight of 10,000 to 25,000 and a crystalline melting point of 493 K.

Nominal tensile strength and flex modulus were determined with conventional compression moulded test specimina and fibres were melt-spun and stretched at a 6:1 ratio. The stretch temperature for the alternating copolymer was 480 K and the melt-spinning temperature was 560 K.

The table below lists the testing results.

Table

	Tensile Strength, MPa		Flex modulus, GPa		Product ITS.IM	Adhesion
	nominal	stretched	nominal	stretched		
N-6^x	30	950	1	5.7	180.5	+ +
PP^x	35	700	1.5	9.2	122.4	+
CE	50	1400	1.4	15.1	302.4	+ + +

^{x} for comparison

Adhesion of the fibres to styrene-butadiene elastomer was determined by testing methods current in the tyre manufacturing industry. The results are represented on a relative scale: + means fair to good, + + stands for very good and + + + is excellent.

Example 2

Copolymer of carbon monoxide, ethylene and propylene of the same batch as used in example 1, is melt-spun at a range of temperatures from 515 to 560 K, via a multi-hole spinneret, quenched with forced air at a temperature of 30 ± 0.5 °C, and stretched 5 to 10-fold. The multi-filaments thus obtained are lightly twisted to yarns, after which 2 or 3 yarns are twined to a cord. These cords are woven to fabrics, which are dipped in adhesive. The fabrics are post-stretched and annealed, thus obtaining fabric cords, presenting attractive adhesion, tensile and flex properties rendering them suitable for use as tyre cords.

Claims

1. A process for producing thermoplastic polymer fibres by melt-spinning, characterized in that an alternating copolymer of an olefinically unsaturated compound and carbon monoxide, having a molecular weight of at least 2000, is melt-spun at a temperature of at least (T + 20) K and the fibre is subsequently stretched at a temperature of at most (T-10) K, in which T is the crystalline melting point of the polymer.

2. A process as claimed in claim 1, in which the melt-spinning temperature is at least (T + 40) K.

3. A process as claimed in claim 1 or 2, in which the stretching temperature is at most (T-25) K.

4. A process as claimed in any of claims 1 to 3, in which the stretching ratio is at least 3:1.

5. A process as claimed in claim 4, in which the stretching ratio is at least 7:1.

6. A process as claimed in any of claims 1 to 5, in which the molecular weight of the polymer is at least 5000.

7. A process as claimed in claim 6 in which the molecular weight of the polymer is at least 8000.

8. A process as claimed in any of claims 1 to 7, in which the copolymer is an ethylene/CO copolymer.

9. A process as claimed in any of claims 1 to 7, in which the copolymer is an ethylene/propylene/CO terpolymer comprising at most 25% mol of propylene in respect of ethylene.

10. A tyre comprising fibres characterized in that they have been produced with a process as claimed in any of claims 1 to 9.